High Temperature Engine Materials: Valve Materials Subtask

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Annual Merit Review

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Project overview

Timeline

- Project start: October 2015
- Project end: September 2020
- Percent complete: 25%

Budget

- Total project funding Received
  - DOE 100%
- FY16 Funding: $ 1,500 K
- Funding anticipated
  FY17: $ 1,500 K

Barriers for Project

Barriers Addressed

- Changing internal combustion engine regimes
- Long lead-times for materials commercialization
- Cost of the high performance alloys

Targets

- Improve passenger vehicle fuel economy by 25%
- Improve commercial vehicle engine efficiency at least 20%

Subtasks

Task 1: High temperature oxidation of exhaust path alloys
Task 2: Modeling high temperature oxidation
Task 3: New alumina-forming alloys for exhaust valves
Task 4: Coatings for exhaust valves
Task 5: LD cast turbo housing alloys (950C)
Task 6: Low cost HD turbo housing alloys (900C)
Task 7: Additive HD turbo compressor wheels
Task 8: Additive manufactured bi-metallic light-weight pistons
Task 9: Lightweight cast superalloys for piston applications

Subtask Overview
New Alumina-forming Alloys for Exhaust Valves

Timeline

- Project start: October 2015
- Project end: September 2019
- Percent complete: 35%

Budget

- Total project funding Received
  - DOE 100%
- FY16 Funding: $ 200K
- Funding anticipated
  FY17: $ 200 K

Barriers

Barriers Addressed

- Changing internal combustion engine regimes
- Long lead-times for materials commercialization
- Cost of the high performance alloys

Targets

- Improve passenger vehicle fuel economy by 25%
- Improve commercial vehicle engine efficiency at least 20%

Industry Advisors/Collaborators

- Lead: ORNL
- Carpenter Technologies- Materials Supplier
- Haynes International-Materials Supplier
- Argonne National Laboratory

Relevance and Objectives

- Exhaust gas temperatures are on the rise and are expected to continue to increase in future high efficiency engines
  - Temperatures are expected to increase from 870^{o}C to 950^{o}C by 2025 and to 1000^{o}C by 2050* in light-duty vehicles

- There is a critical need to develop materials that meet projected operational performance parameters but meet *cost constraints*

- Objectives: Develop cost-effective exhaust valve materials suitable for operating at temperatures up to 950^{o}C for use in advanced future engine concepts
  - Mechanical properties are a f(cylinder pressure, valve diameter, temp)
  - Oxidation resistance is critical

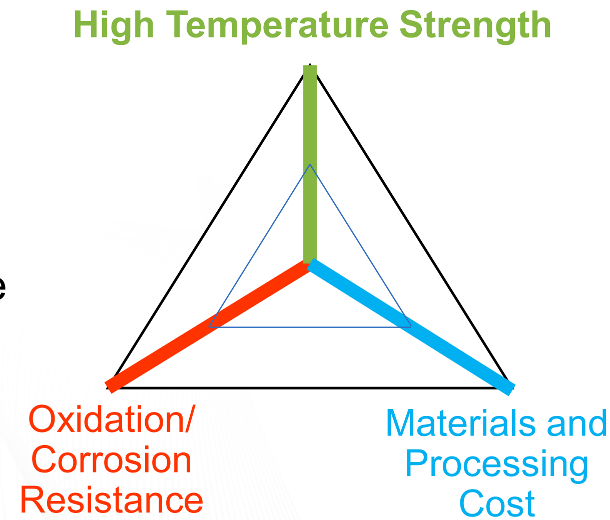
***DOE Vehicle Technologies Workshop report: Light-Duty Vehicles Technical Requirements and Gaps for Lightweight and Propulsion materials, Feb. 2013**

FY16-FY17 Milestones

Month/ Year	Milestone Description	Status
March 2016	Using computational modeling, identify alloying element additions with the potential to increase strengthening phase fraction at 950°C by 15 % relative to existing alumina forming alloys	Completed
Dec. 2016	Complete fabrication of initial laboratory scale heats of new alumina-forming alloys with increased strength capability at 950 °C	Completed
Sep. 2017	Down-select two alloys with the potential for at least 10% improvement in strength at 950 °C operation compared to commercial alloy Haynes®224 and good oxidation resistance	On-Track

Approach

- Current baseline commercial valve alloy 751, a chromia-forming alloy is
  – Primarily strengthened by coherent, intermetallic precipitates- γ' ($Ni_3(Al,Ti,Nb)$)
  – Does not have significant strength above ~850^{o}C due to dissolution of strengthening phase
- A previous project developed lower cost chromia-forming alloys for use at 870 °C
- Current project aims to extend work to develop lower cost alloys for use at 950 °C
  – Strength decreases significantly at 950 °C
  – Oxidation behavior limits alloy design and performance
  – Alloy properties must be achieved at lowest cost



- Overall approach to alloy development:
  – Achieve a stable, chromia or alumina scale for good oxidation resistance
  – Improve strength by increasing volume fraction and modifying other desirable characteristics (coherency etc.) of strengthening phases at 950 °C

Chromia-Forming, Commercial Ni-Based Alloys and their Compositions

Alloy	Ni	Co	Fe	Cr	Mo	Si	Al	Nb	Ti	W	C	Matl cost Low Ni	Matl Cost High Ni	Man. cost
IN® 751	**71.3**	**0.0**	**8.0**	**15.7**	**-**	**0.09**	**1.2**	**0.9**	**2.6**	**-**	**0.03**	**1**	**1**	+
Nimonic® 80A	75.6	0.1	0.5	19.6	-	0.1	1.4	-	2.5	-	0.08	**1.1**	**1.1**	+
Rene® 41	56.0	10.6	0.2	18.4	9.9	0.0	1.6	-	3.2	-	0.06	**1.5**	**1.3**	++
Udimet ® 520	**57.7**	**11.7**	**0.6**	**18.6**	**6.35**	**0.1**	**2.0**	**-**	**3.0**		**0.04**	**1.5**	**1.3**	+++
Udimet® 720	57.3	14.8	0.1	15.9	3.0	0.0	2.5	0.0	5.1	1.2	0.01	**1.6**	**1.4**	+++
Nimonic® 90	59.7	16.1	0.5	19.4	0.1	0.2	1.4	0.0	2.4	-	0.07	**1.7**	**1.4**	+
Cost $/Kg	**12.6 - 19.8**	**55.4**	**0.210**	**10.9**	**17.8**	**2.7**	**1.9**	**42**	**9.9**	**33.6**				

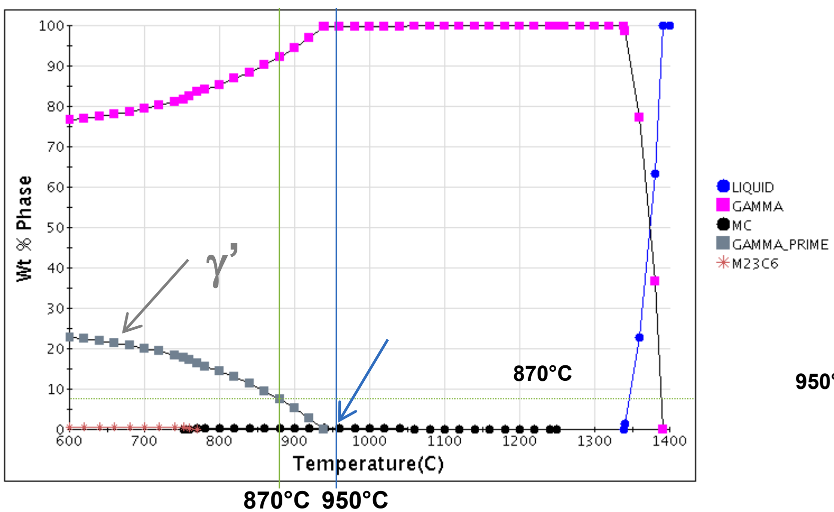
- Alloys contain high Cr to form chromia-scale
- Mechanical strength, oxidation resistance, and COST are major factors

Computational Thermodynamics Predictions are Used to Guide Alloy Development

Two major steps are used in new alloy development:

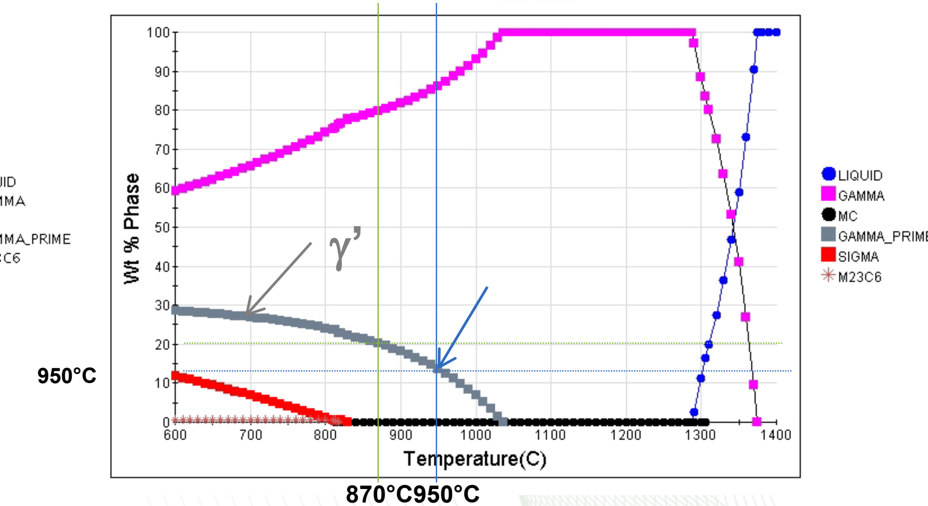
- **Oxidation testing at temperatures up to 950°C- Predictive model NOT available**
- **Identify alloys with required γ' content and other precipitate properties (precipitate size, precipitate size distribution, lattice misfit, Anti-Phase Boundary Energy (APB))**

Current Alloy - 751



No γ' at 950°C Y. S. at 950°C: ~19KSi

Typical New ORNL Alloy



γ' present at 950°C, Y. S. at 950°C:~43 Ksi

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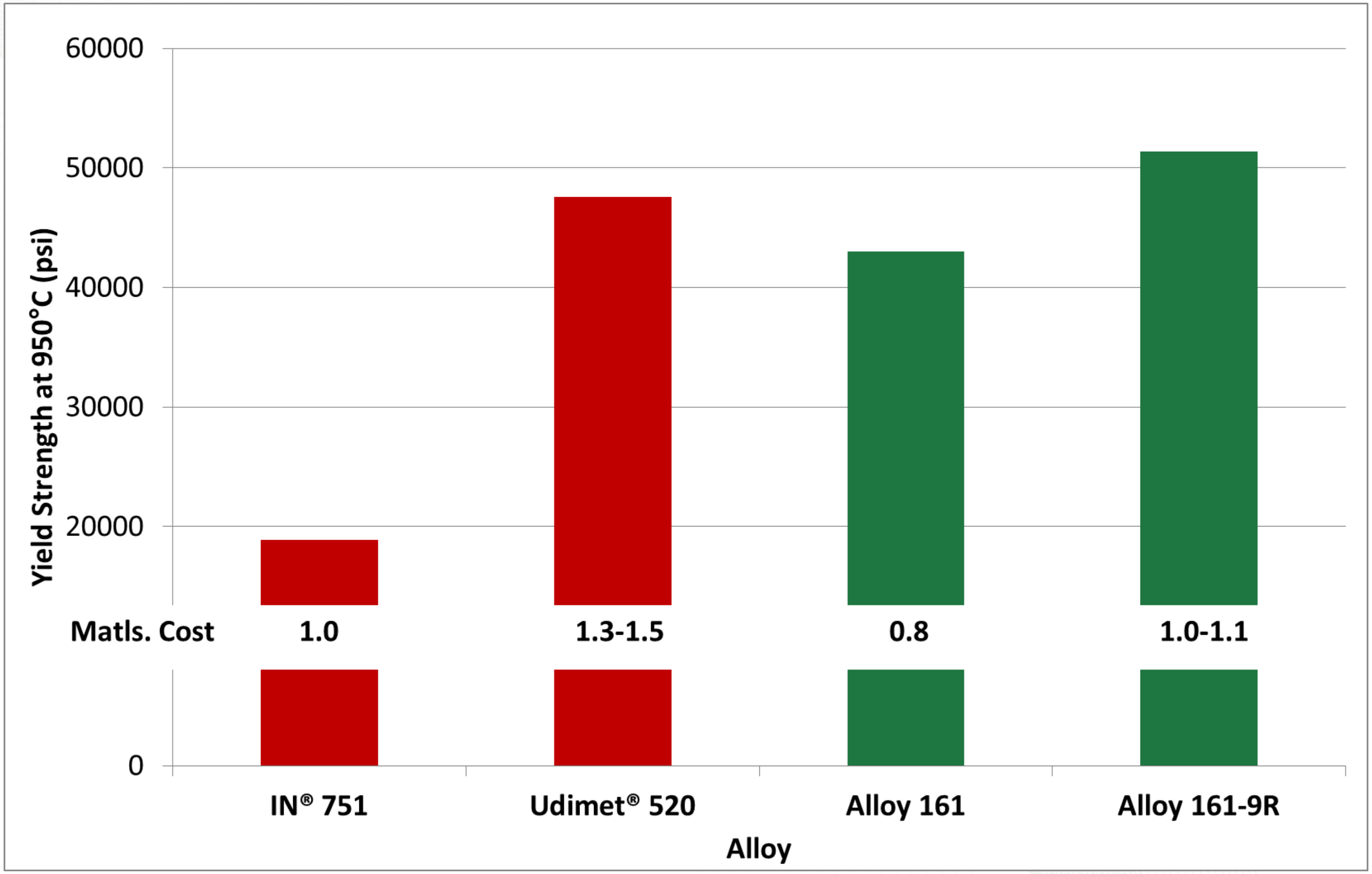
Previous Accomplishments and Progress: High-Strength, Lower-Cost, Chromia-Forming Alloys Have Been Developed for 950°C



- **Strength greater than that of Udimet ®520 achieved at lower cost**

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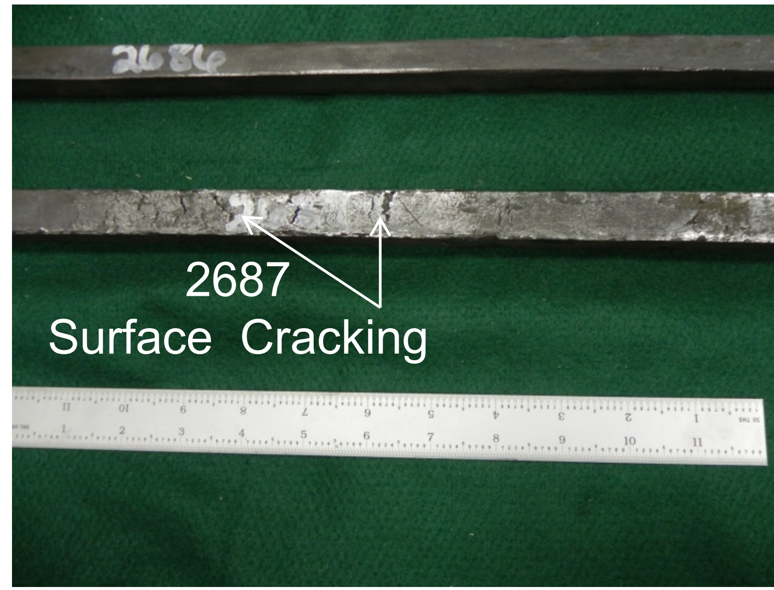
Accomplishments: Gleeble Testing Identifies Better Processing Window for High-Strength ORNL Alloy

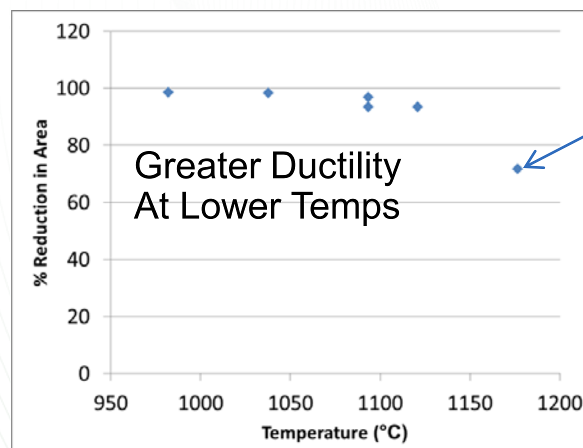
- Surface cracking observed in high strength alloy Heat # 2687 (47Ni-18Cr- Al-Ti)
  - Process modifications have been suggested by Carpenter

- Gleeble testing shows lower process temperatures are better

- New industrial scale heat is planned

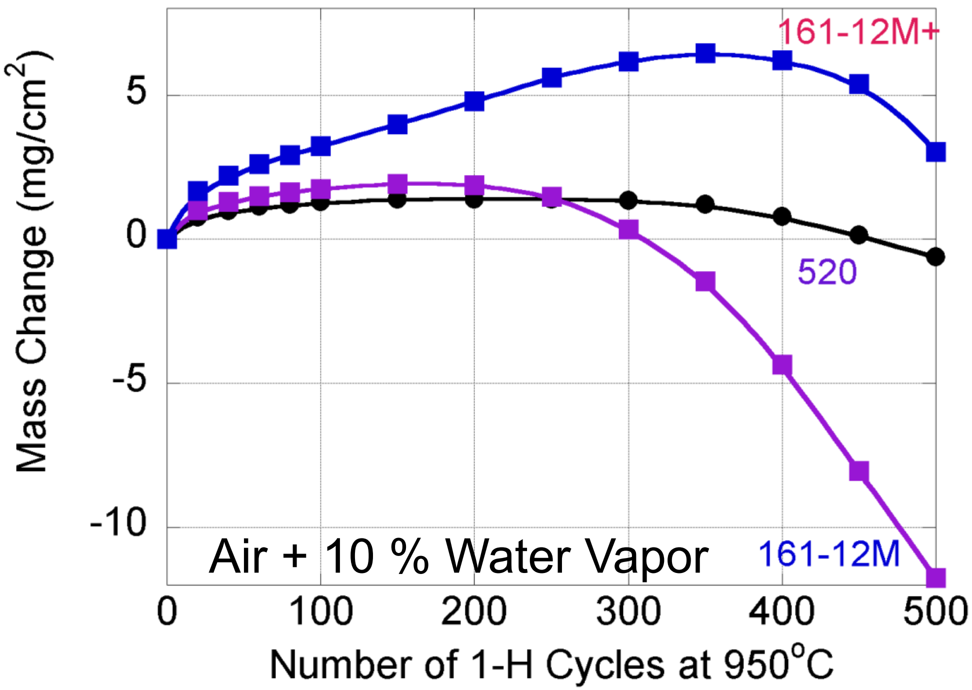
2686
No cracking

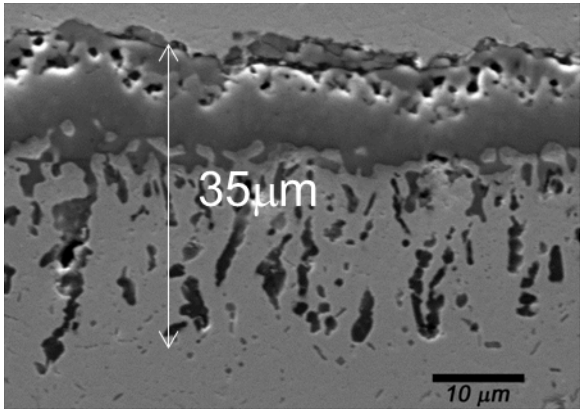




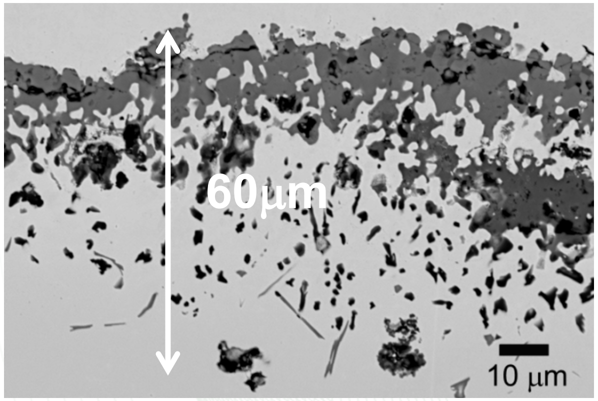
Current Processing Temp

Drawback of Chromia-Formers: Thick Oxide Scales and Internal Oxides Form at 950°C and Begin To Spall*





161-12M+ ORNL Alloy 200 hours



Udimet®520 after 500 hours

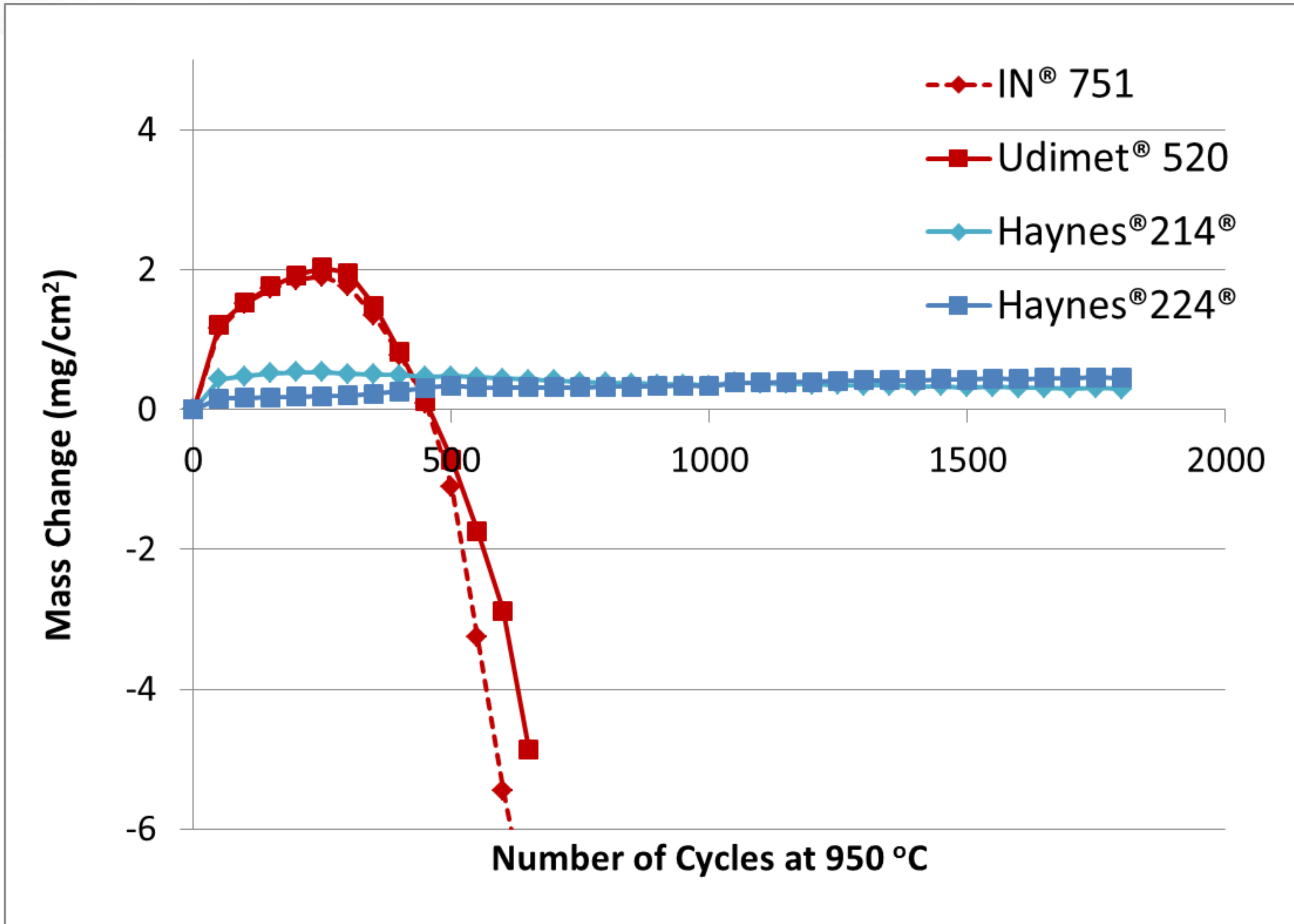
*Collaboration with Bruce Pint and Allen Haynes, ORNL

Alternatives: Alumina-Forming, Ni-Based Alloys

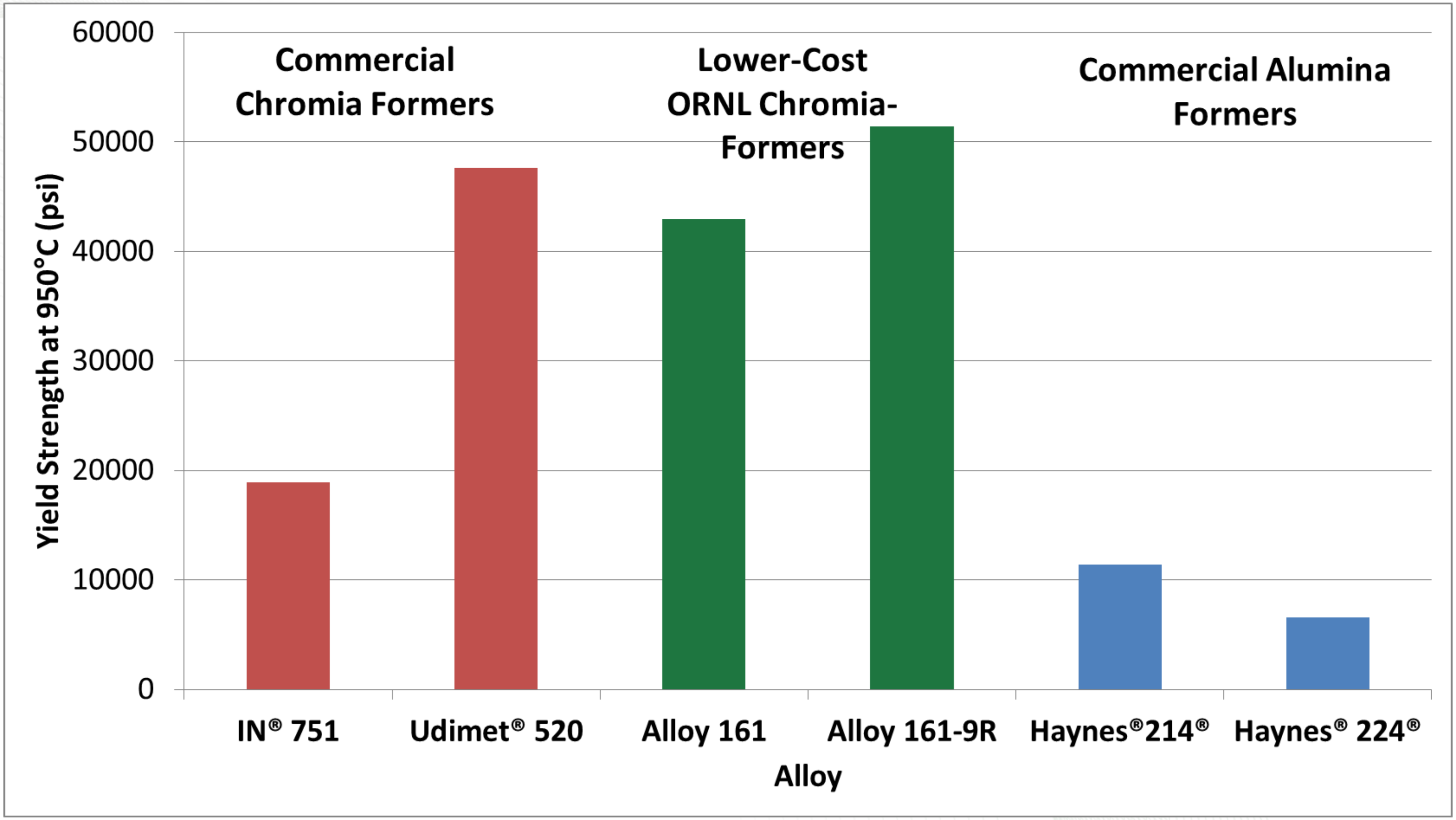
Alloy	Ni	Co	Fe	Cr	Mo	Si	Mn	Al	Ti	W	C	Comments
IN ® 751	71.32	0.04	8.03	15.7	-	0.09	0.08	1.2	2.56	-	0.03	Chromia-former
Udimet® 520	57.65	11.7	0.59	18.6	6.35	0.05	0.01	2.0	3.0	-	0.04	Chromia-former
Haynes® 214®	72.3	<0.15	3	16	<0.2	0.07	<0.5	4.5	<0.5	<0.5	0.04	Alumina-former
Haynes® 224®	44.75	<2	27.5	20	<0.5	0.3	<0.5	3.6	0.3	<0.5	0.05	Alumina-former

- Alumina-formers contain Cr + high Al
  - Increase oxidation resistance
  - Lowers strength due to high Al in γ'
- Technical goal
  - Stronger, alumina-forming alloys

Commercial Alumina-Forming Alloys Show Excellent Oxidation Resistance at 950°C

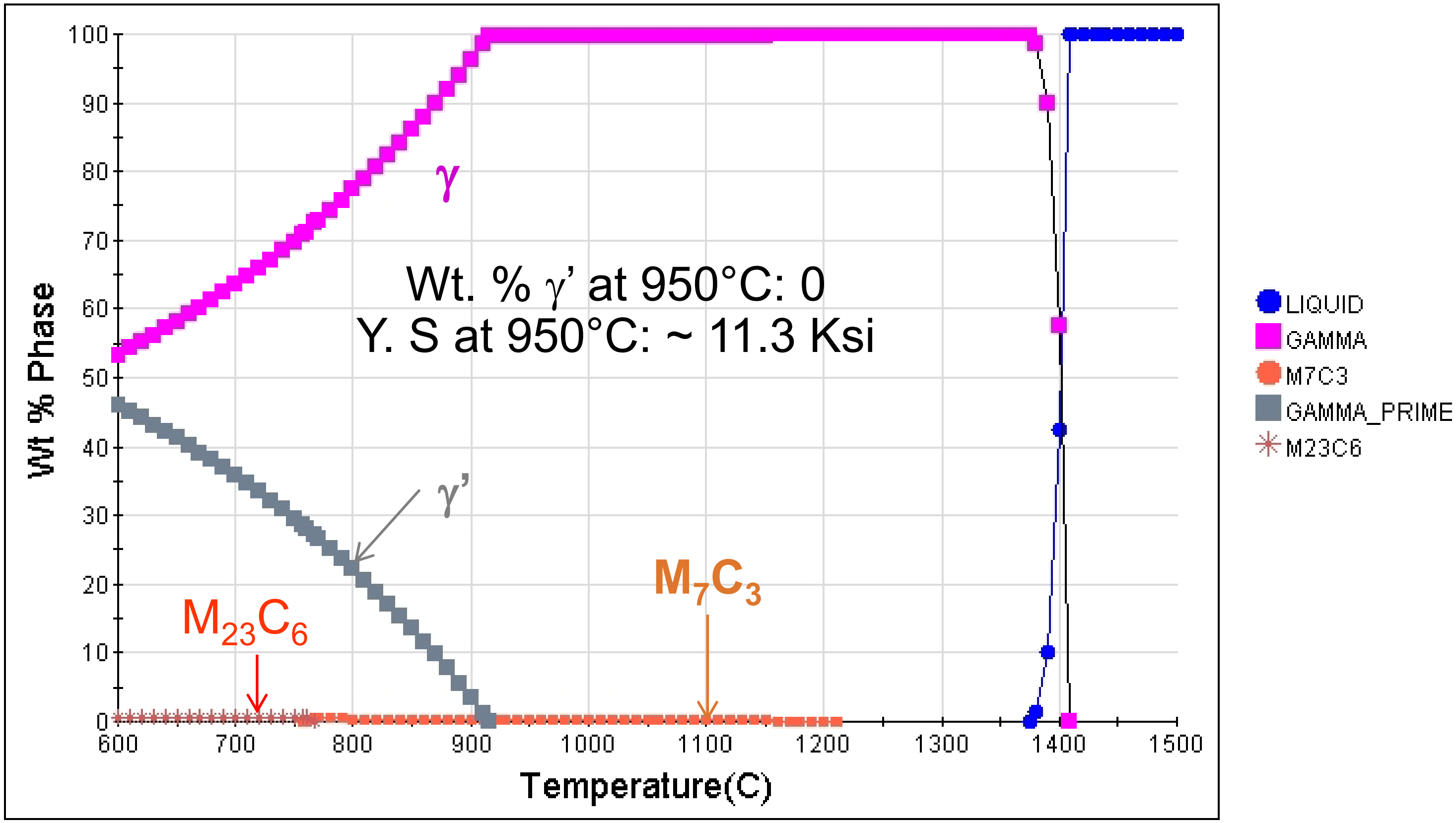


Use of Commercial Alumina-Forming Alloys at 950°C May be Limited by Strength

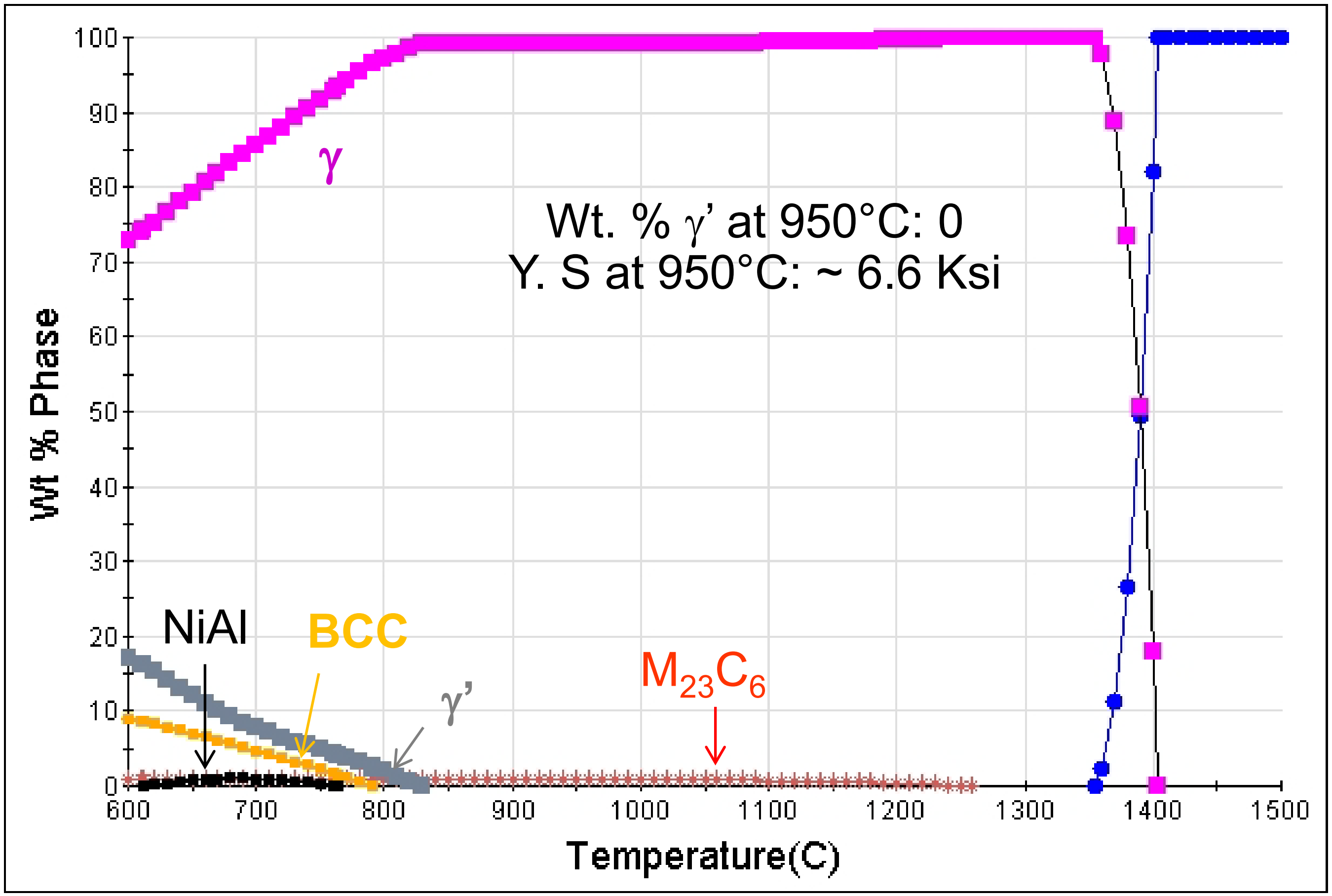


Strength of commercial alumina-forming alloys lower than that of higher performance chromia-forming alloys (Udimet ®520)

Haynes®214® Has High Ni (72.3 wt. %) But Lacks Strength at 950°C



Haynes®224® Has Low Ni and Has No γ' at 950°C



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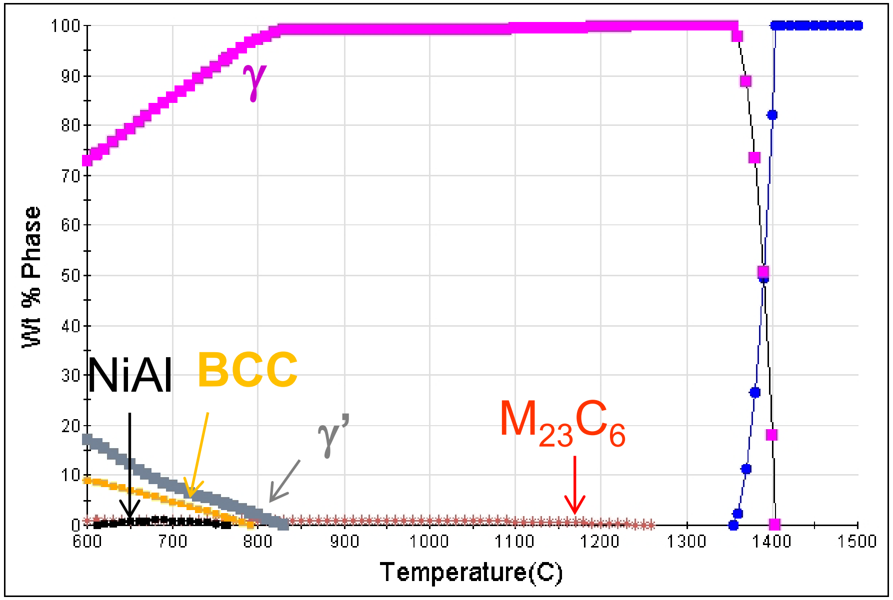
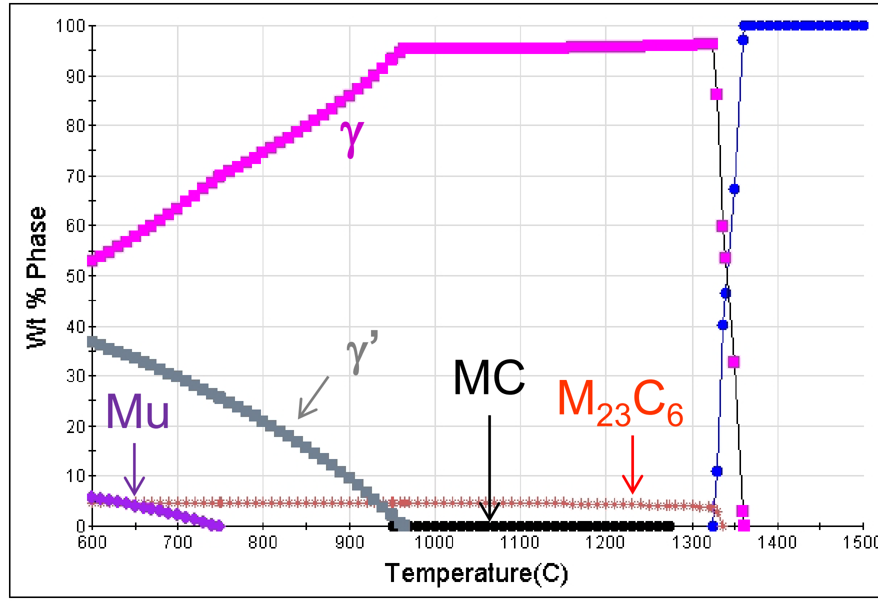
New ORNL Alloys Have Greater Amount of Strengthening Phases at 950°C



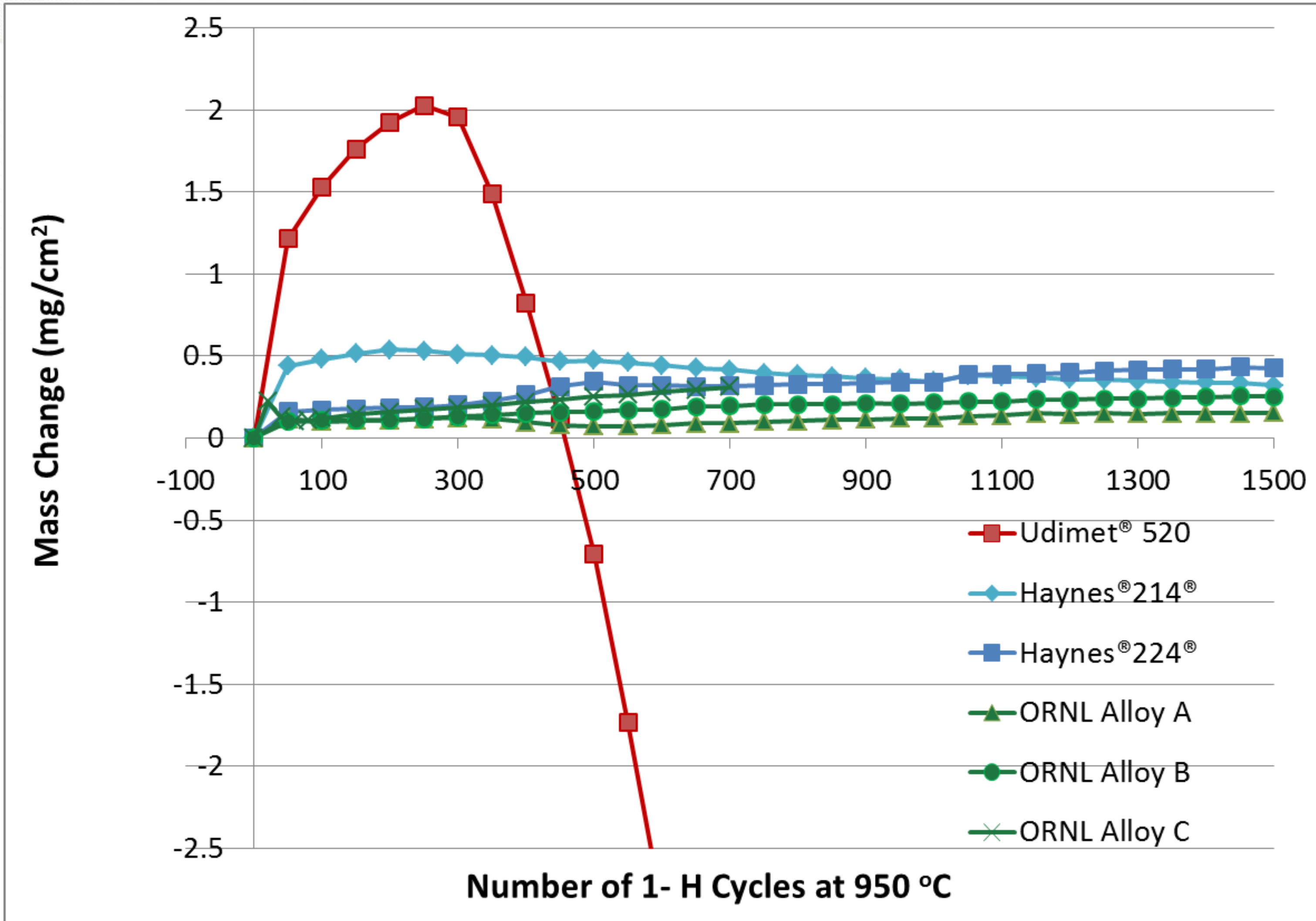
Haynes®224®

Wt. % γ' at 950°C: 0
Y. S at 950°C: ~ 6.6 Ksi

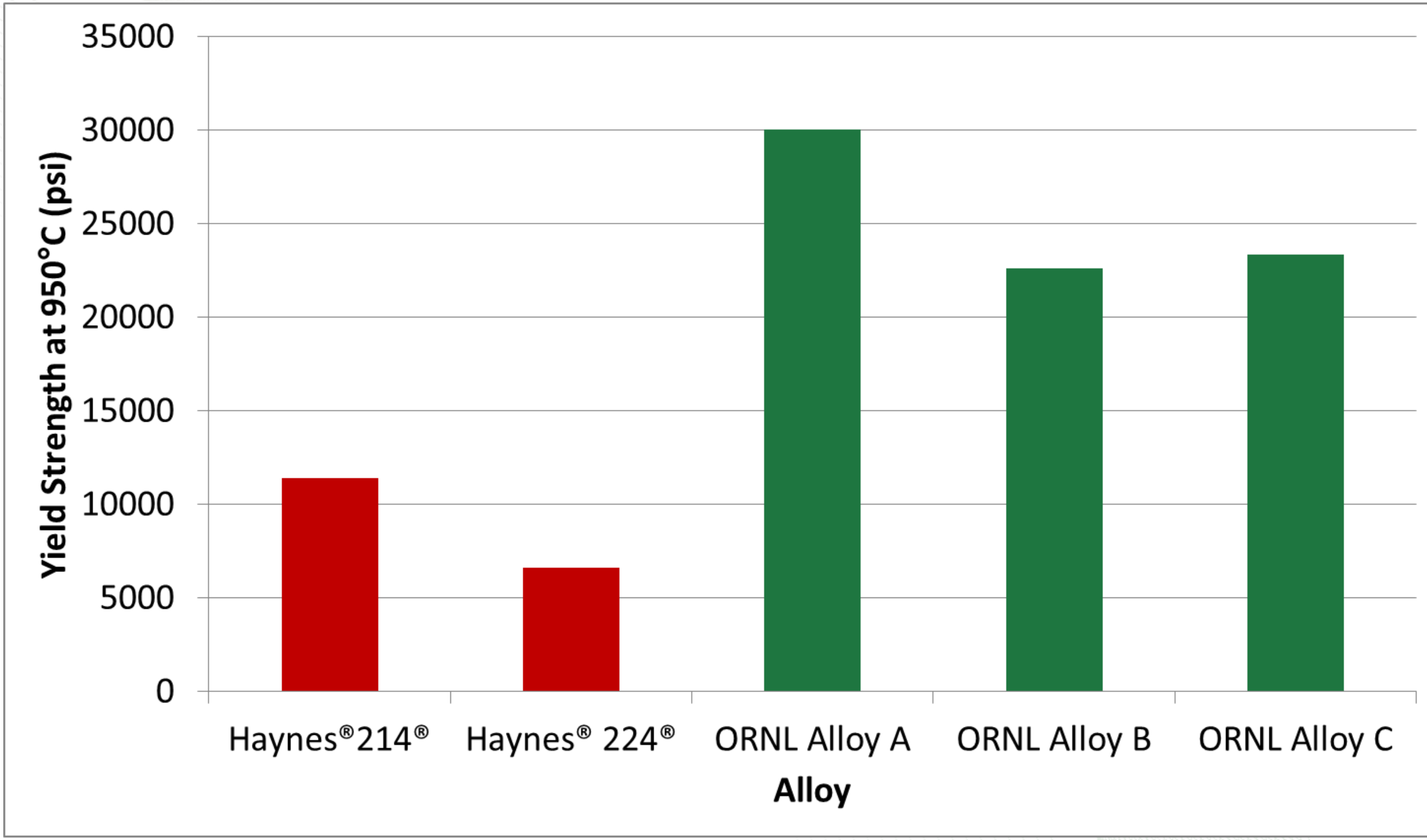


ORNL Alloy B
Wt. % γ' at 950°C: ~ 2.5 wt. %
Y. S at 950°C: ~ 23 Ksi

New ORNL Alloys have Excellent Oxidation Resistance at 950°C



New ORNL Alumina-Forming Alloys Have Higher Strength at 950°C



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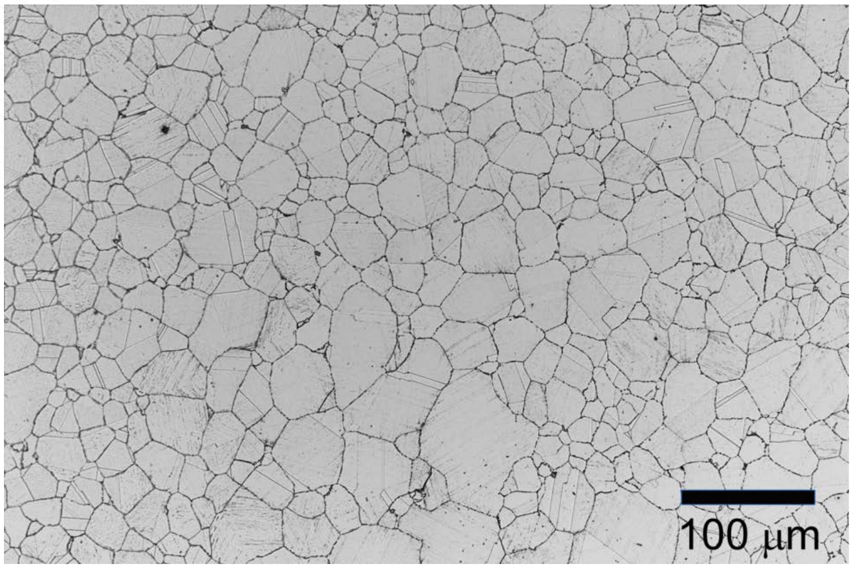
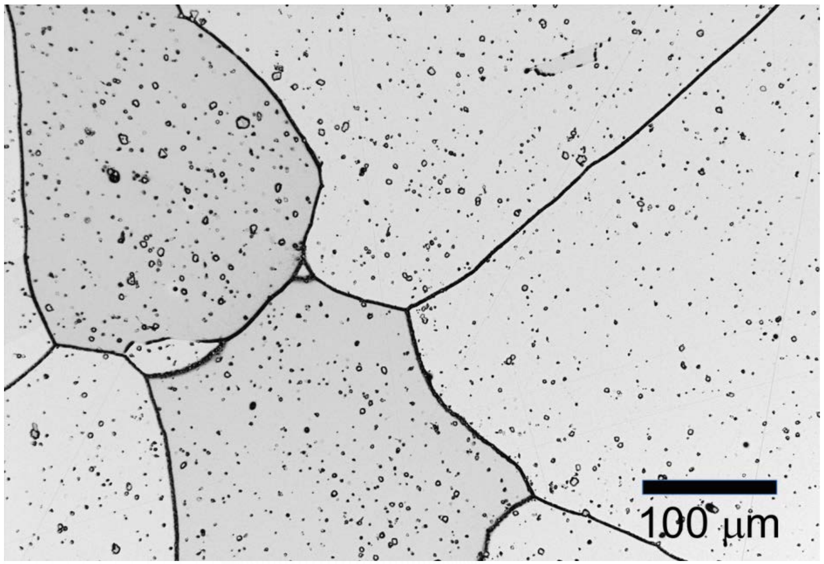
Tensile Properties of New ORNL Alloys Can be Further Improved with Microstructure Modifications



Haynes®214®



ORNL Alloy C

Heat-treatment strategies to control grain size and improve high temperature mechanical properties are in development

Collaborations and Coordination with Other Institutions

- New US Patent (US 9,605,565 B2) has been granted to ORNL from prior project on chromia-forming alloys for 870°C
- Collaborations are on-going with Carpenter Technologies
  - Gleeble test conditions and procedures relevant to industrial processing of alloys were provided
  - New heat is planned with revised processing parameters
- Collaborations with Haynes Technologies
  - Materials (Haynes®214® and Haynes®224®) supplied by Haynes
  - Feedback received on best heat-treatment conditions and measured properties
    - Aging heat-treatment of 4 hours at 800°C – down-selected heat-treatment
- Collaborations with Argonne National Laboratory are on-going
  - Extended range Ultra Small-angle, Small-angle, and Wide-angle X-ray scattering facility for particle size and particle size distribution
  - Powder diffraction facility for structure characterization

Response to Reviewer's Comments

This project was not reviewed last year

Remaining Challenges and Barriers

- Further improvement in yield strength at 950°C must be achieved to be competitive with chromia-formers
- Increase in yield strength must be achieved without loss of oxidation resistance
- Alloys must be evaluated for industrial scale processing
- Good strength and oxidation resistance must be achieved in alloys processed in industrial scale

Proposed Future Research

FY17-FY18

- Heat-treatment and processing steps will be modified to achieve microstructure that balances strength and ductility
- Increased additions of alloy elements will be considered to improve high temperature strength
- Down-select most promising alloy
- Work with industrial adviser/industrial partner to produce trial heats in industrial scale

Any proposed future work is subject to change based on funding levels

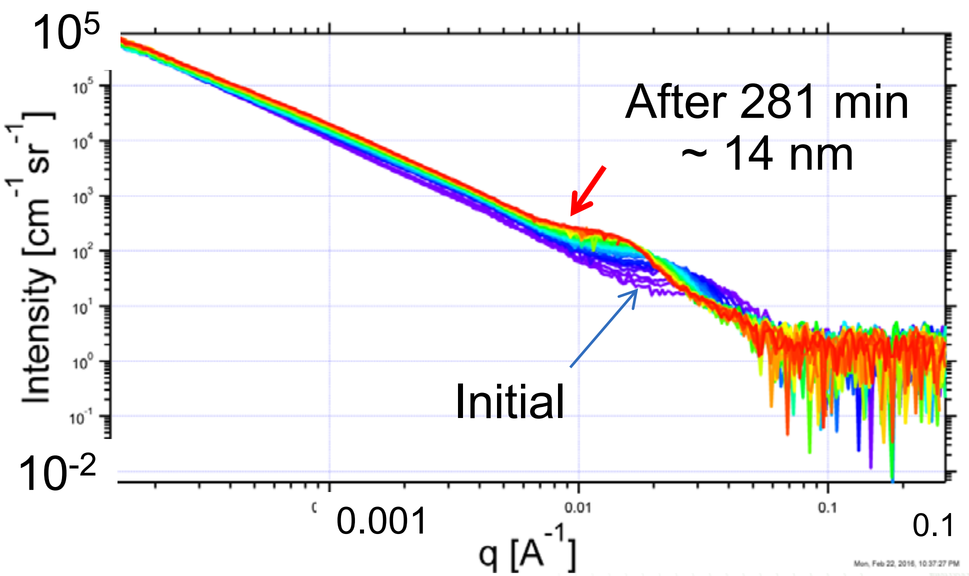
Summary

- **Relevance:**
  - Temperatures are expected to increase from 870^{o}C to 950^{o}C in 2025 and to 1000^{o}C by 2050 in light-duty engines. Current valve alloy cannot meet strength and oxidation requirements for use at the higher temperatures and new cost-effect materials are needed for use at these temperatures.
- **Approach/Strategy**:
  - A computationally guided approach is being used to develop new higher strength alumina-forming alloys for use at 950^{o}C. A similar approach has been used previously to develop new cost-effective chormia-forming alloys for use at temperatures up to 950^{o}C.
- **Accomplishments:**
  - New alumina-forming alloys with oxidation resistance comparable to commercial alumina-forming alloys but with greater yield strength at 950^{o}C have been developed.
- **Collaborations:**
  - Collaborations are on-going with Carpenter Technologies, Haynes International, and Argonne National Laboratory
- **Proposed Future Work:**
  - Heat-treatment strategies to control grain size and improve high temperature mechanical properties are in development. Effect of increase in alloying element additions will be evaluated and new compositions will be developed.

Back-up Technical Slides

In-situ USAXS/SAXS showing particle size Evolution in Haynes 214 at 800°C*

- *In-situ* Extended range Ultra Small-angle Scattering, and Small-angle scattering (USAXS/SAXS) is used to characterize γ' precipitate size after heat-treatment and its evolution during use
- High resolution powder diffraction is used to measure lattice misfit between γ and γ'
- Data can be used in alloy design and heat-treatment to achieve higher strength



*Collaboration with Ross Andrews and Jan Ilavksy, Argonne National Laboratory